



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>4</sup> :  B01J 35/10, 21/16, 29/28		A1	(11) International Publication Number: WO 85/03241  (43) International Publication Date: 1 August 1985 (01.08.85)
<p>(21) International Application Number: PCT/SE85/00037</p> <p>(22) International Filing Date: 29 January 1985 (29.01.85)</p> <p>(31) Priority Application Numbers: 8400427-4 8400429-0 8400432-4 8400433-2</p> <p>(32) Priority Dates: 30 January 1984 (30.01.84) 30 January 1984 (30.01.84) 30 January 1984 (30.01.84) 30 January 1984 (30.01.84)</p> <p>(33) Priority Country: SE</p> <p>(71) Applicant (for all designated States except US): EKA AB [SE/SE]; S-445 01 Surte (SE).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only) : OTTERSTEDT, Jan-Erik, Anders [SE/SE]; Åsabacken 51, S-445 00 Surte (SE). BAEZA CALZADILLA, José, Aurelio [SE/SE]; Skogsgläntan 70, S-435 00 Mölnlycke (SE). DAHLQVIST, Per-Arne [SE/SE]; Trätte Hedra, Pl 4190, S-440 92 Svanesund (SE). JÄRÅS, Sven, Gunnar [SE/SE]; Kornvägen 9, S-442 39 Kungälv (SE). RÖJ, Jan-Anders, Olav [SE/SE]; Klövervägen 11, S-442 39 Kungälv (SE)</p>		<p>(74) Agent: AWAPATENT AB; Box 5117, S-200 71 Malmö (SE).</p> <p>(81) Designated States: AT (European patent), BE (European patent), BR, CH (European patent), DE (European patent), DK, FI, FR (European patent), GB (European patent), JP, LU (European patent), NL (European patent), NO, SE (European patent), US.</p> <p><b>Published</b> <i>With international search report. In English translation (filed in Swedish).</i></p>	

(54) Title: FILLER OR A SUPPORT FOR CATALYTICALLY ACTIVE SUBSTANCES, A PROCESS FOR PRODUCING SAID FILLER OR SUPPORT, A CATALYST PRODUCED FROM SAID SUPPORT, AND THE USE OF SAID CATALYST

## (57) Abstract

A filler or support for catalytically active substances consists of aggregate particles having a coherent three-dimensional network structure of mineral particles having fibrous or strip-shaped structure and a diameter of at least 100 Å and a mechanical, thermal and hydrothermal stability required for hydroprocessing or hydrogenation. The support has a surface area of at least 75 m<sup>2</sup>/g and an average pore diameter of at least 100 Å, at least 75% of the surface area being in pores having a diameter exceeding 100 Å. In a hydroprocessing, hydrogenation or cracking catalyst, the catalytically active substance is deposited in the form of a surface coating on the fibrous or strip-shaped mineral particles of the support. As fibrous or strip-shaped mineral particles may be made of attapulgite, sepiolite and chrysotile. The filler or support is produced by forming a well-dispersed slurry of mineral particles which, in the natural state, have the requisite particle diameter or to which this particle diameter has first been imparted by modification, whereupon the well-dispersed slurry either is spray-dried in order directly to form the aggregate particle or is extruded or pelletised to form such aggregated particles, or is first spray-dried to aggregate particles which are then slurried and extruded or pelletised to the desired catalyst support particles, the catalytically active substance being applied, in the production of the catalyst, in the form of a surface coating on the fibrous or strip-shaped particles of the support prior to or after spray-drying, extrusion or pelletisation of the support particles.

BEST AVAILABLE COPY

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT Austria  
AU Australia  
BB Barbados  
BE Belgium  
BG Bulgaria  
BR Brazil  
CF Central African Republic  
CG Congo  
CH Switzerland  
CM Cameroon  
DE Germany, Federal Republic of  
DK Denmark  
FI Finland  
FR France

GA Gabon  
GB United Kingdom  
HU Hungary  
IT Italy  
JP Japan  
KP Democratic People's Republic  
of Korea  
KR Republic of Korea  
LI Liechtenstein  
LK Sri Lanka  
LU Luxembourg  
MC Monaco  
MG Madagascar  
ML Mali

MR Mauritania  
MW Malawi  
NL Netherlands  
NO Norway  
RO Romania  
SD Sudan  
SE Sweden  
SN Senegal  
SU Soviet Union  
TD Chad  
TG Togo  
US United States of America

FILLER OR A SUPPORT FOR CATALYTICALLY ACTIVE SUBSTANCES, A  
PROCESS FOR PRODUCING SAID FILLER OR SUPPORT, A CATALYST  
PRODUCED FROM SAID SUPPORT, AND THE USE OF  
SAID CATALYST

In catalytic processes, one frequently has to rely on rapid mass transportation in combination with a high accessibility of the catalytically active surface in order to achieve high reaction yield, good 5 selectivity and thus satisfactory economy of process.

The refining of heavy oils into different fuels, such as gasoline and diesel, is carried out by means of catalytic processes, for example catalytic hydroprocessing, hydrogenation or cracking. As a result of 10 the increased crude prices, it is endeavoured to catalyse increasingly heavier starting materials, and this has made it difficult to achieve a satisfactory economy of process because a combination of rapid mass transportation and high accessibility of the 15 catalytically active surface is not readily accomplished. The heavy starting materials, in particular residual fractions, are characterised in that they have large molecules and aggregates of large molecules, for which reason it is difficult to achieve a rapid 20 transport of these molecules or molecule aggregates into and out of the catalysts which are being used today for catalytic hydroprocessing, hydrogenation or cracking. Another problem encountered in connection with catalytic cracking is that the most common 25 catalyst supports have but low resistance to the process conditions and the conditions during the regeneration and like treatment processes to which the catalyst must be subjected.

Another field in which problems are caused by 30 prior art supports for catalytically active substances, is the catalytic automobile exhaust emission control, i.e. a purification process in which it is desired

to remove nitrogen oxides and non-burned hydrocarbon molecules from the exhaust gases from automobile engines and other internal combustion engines. In this case, the difficulty lies not in large molecules, but instead 5 in the need for very high exhaust throughflow rates in the catalytic reactor. Great demands are therefore placed on the porosity in combination with a large catalytic area, such that the catalytic reactions which are necessary in order to eliminate nitrogen 10 oxides and non-burned hydrocarbons, can take place in the very short time during which the exhaust gases are in contact with the catalyst mass.

Catalytic cracking of heavy oils to gasoline and diesel is an example of a refinery process in 15 which the process economy to a high degree is affected by the presence of large molecules and aggregates of molecules in the oil. One of the difficulties with heavy molecules and aggregates of molecules in the oil is that these frequently contain metal impurities 20 of the type vanadium and nickel which have an adverse effect on the activity and selectivity of the catalyst. The above-mentioned problem in respect of rapid mass transportation of the large molecules or molecule aggregates into the interior of the catalyst structure 25 causes in itself a further problem in connection with catalytic cracking. The diffusion rates of the large molecules and aggregates of molecules can be so low that the molecules stay too long in the catalyst and thus are subjected to so-called overcracking into 30 undesired products, such as gases and coke. A further problem encountered in catalytic cracking of heavy oils of the type residual oils is that the largest molecules and molecule aggregates easily get stuck in the small pores of the catalyst and are not removed 35 during the so-called stripping step which, in the refinery process, precedes the regeneration. As a result, many large molecules and molecule aggregates

may be taken along by the catalyst to the regenerator where they are burned and thus will be lost, the temperature in the regenerator increasing to undesired high values. The large molecules or molecule aggregates 5 getting stuck in the pores within the outer parts of the catalyst may also have the effect that the activity and efficiency of the catalyst is reduced considerably because subsequent molecules, both large and small ones, are prevented from penetrating into 10 the active surface of the catalyst for cracking.

As regards the catalytic hydroprocessing of heavy oils, one has, in order to remove metal impurities and hetero atoms such as nitrogen and sulphur, from the oil, increased the mass transportation of oil 15 into and out of the catalyst by increasing the average pore size of the catalyst. In conventional hydroprocessing, for example desulphurisation of gasoline and diesel fractions, use is made of catalysts which consist of aluminium oxide having pore sizes within 20 a rather narrow range of 40-70 Å. The porous aluminium oxide usually is impregnated with a mixture of, for example, cobalt sulphide and molybdenum sulphide. This type of catalyst functions satisfactorily for the removal of sulphur from the light molecules present 25 in the relatively light hydrocarbons in gasoline and diesel. As regards the removal of metals, sulphur and nitrogen from the heavy molecules occurring in, for example, heavy fuel oils and residual fractions, the activity and efficiency of conventional hydroprocessing catalysts is reduced considerably because 30 large molecules or molecule aggregates get stuck in the pores within the outer portions of the catalyst so that subsequent molecules, both large and small ones are prevented from penetrating into the active 35 surface of the catalyst for hydroprocessing.

One way of coping with this problem in connection with cracking and hydroprocessing catalysts has been to produce catalyst structures having a larger average pore size. Efficient cracking or hydroprocessing of, 5 for example, heavy fuel oils, requires a catalyst structure having an average pore size exceeding 200 Å. There is no difficulty in producing such structures from, for example, aluminium oxide or zeolites; instead, the difficulty lies in obtaining in such a 10 structure a high surface area within pores that are so large (larger than 100 Å pore diameter) that the large molecules or molecule aggregates can be readily and rapidly transported to the catalytically active surface within the pores, which is necessary in order 15 to achieve high catalytic activity. The surface area of the catalyst support is in the inverse ratio to the average pore size in such a conventional catalyst. A conventional catalyst, e.g. a desulphurisation catalyst, may have an average particle size of about 40 20 Å and a surface area of about 150 m<sup>2</sup>/g. If the average pore size of such a conventional catalyst is increased to 200 Å, the surface area, on the other hand, will be reduced drastically to about 50 m<sup>2</sup>/g of catalyst material. In the refinery industry, however, it is 25 desired to be able to use catalysts, e.g. a hydroprocessing catalyst, having an average particle size exceeding 200 Å because one has found that the average pore size should be at least 10 times greater than the average diameter of the large molecules or molecule aggregates which are to pass into and out of the pores. 30

For catalysts for catalytic cracking of oils, use is made of a support containing an active component which frequently is zeolite Y in hydrogen form or in the form of a rare earth metal, said active 35 component being embedded in a matrix which may consist of, for example, kaolin and which contains a binder in the form of a silicate or an aluminium sili-

cate gel. The active component, i.e. the zeolite, has a very regular pore structure and is characterised by pores in the order of 12 Å with pore openings in the order of 7-8 Å. The matrix in which the active component is incorporated, may have a pore structure varying from some twenty Ångström up to several thousand Ångström. Recently, the development of cracking catalysts has tended to reduce the proportion of binder (which consists of silicic acid gel or an aluminium silicate gel), thereby to reduce the proportion of fine pores in the catalyst and thus the difficulties associated with the penetration of large molecules into small pores. In the catalytic cracking of heavy oils, it has been tried to avoid these problems by first subjecting the oil to a separate preliminary cracking utilising a catalyst which consists solely of spray-dried and calcined kaolin, i.e. a catalyst which does not contain zeolite or binder. The catalyst of such a pre-cracking step has a high average pore size and, thus, also a low surface area. In the pre-cracking step, a large proportion of the content of metallic impurities in the heavy oil is removed. After this pre-cracking, cracking with a conventional cracking catalyst is carried out. However, this solution to the problem requires additional cracking reactors. A further technique of solving the problem in connection with the catalytic cracking of heavy oils is to use zeolitic structures of larger pores and pore openings than are available in zeolite Y. In this case, use is made of clays having a plate-like structure, such as montmorillonite clays (cf. US-A-4,238,364). These plates have been bonded together by means of crosslinks in the order of 10 Å. The spacing between the crosslinks may be varied, but lies typically at about 20 Å. Montmorillonite which is cross-linked in this manner, is characterised by pore openings which are about 10 Å in one direction and about 20 Å in the other

direction, i.e. considerably larger than in zeolite Y, but still rather small as compared to the dimensions of the largest molecules in heavy oils.

According to DE-C2-3003361 a catalyst material 5 is produced by first forming a gel by mixing together an inorganic aluminium salt and an alkali metal silicate as well as a water-soluble anionic polyacrylic amide. To this gel is then added an aqueous dispersion of a zeolitic crystalline aluminium silicate, whereupon 10 the whole of it is spray-dried at a temperature causing a degradation of the polyacrylic amide. The catalyst material obtained is not, however, based on a mineral having fibrous structure.

According to DE-B2-1542185 a zeolite-containing 15 cracking catalyst is produced by forming a slurry of clay material or silica/aluminium oxide and other materials, whereupon the zeolite material is admixed. After filtration and drying, an ion exchange is effected. Drying may be done by spray-drying, but the resulting 20 catalyst material is not based on a mineral of fibrous structure.

GB-A-1485370 discloses a catalyst which is made from "KAOWOOL" which is a mineral fibre product having coarse fibres which presumably are at least 0.1 mm 25 thick. Such a batting structure or fibre structure cannot be used for the production of a support or catalyst of the type here concerned.

GB-A-2090766, on the other hand, discloses a porous hydroprocessing catalyst based on halloysite. 30 This catalyst is produced by preparing two dispersions of different mineral materials and then converting these dispersions into catalyst support particles which are coated with a catalytically active substance. When catalyst support particles are being shaped, 35 the tubular halloysite fibres have a tendency to realignment, which causes an unsatisfactory pore structure and distribution in the finished catalyst support

particle. For this reason, this patent specification suggests the admixture of other types of fibres which are thinner than the halloysite fibres. These thinner fibres give stability to the fibre structure of the catalyst support particles during shaping. The resulting catalyst support particles have a relatively large pore diameter of 200-700 Å, but it was found that such a catalyst support has a relatively low surface area detrimental to the catalyst activity. Usually, the BET surface area lies about  $50 \text{ m}^2/\text{g}$ . A probable explanation is that the halloysite fibres have a smooth surface structure. As mentioned above, it is necessary, in processing especially heavy hydrocarbon fractions and residual fractions, to have large pores in combination with a high activity, and the high activity is best obtained with a large surface area, in spite of the large pores.

Another problem which is encountered in the hydroprocessing of heavy oils, and which is especially pronounced in connection therewith, is the handling of spent catalysts. For example, hydroprocessing catalysts contain not only the catalytically active metals, such as cobalt and molybdenum, which are initially present in the catalysts, but also large amounts (up to several per cent) of metallic impurities of the type vanadium and nickel. In many parts of the world, the deposition of spent catalysts in landfills is deemed to constitute an environmental hazard. An alternative is then to remove the metals, i.e. both the catalytically active metals and the metallic impurities, from the catalyst support prior to deposition. This can be done for example by leaching the spent catalyst with acids of the type sulphuric acid, but this means that also the support which usually consists of aluminium oxide, will be dissolved in the acid, resulting in, on the one hand, high chemical costs and, on the other hand, difficulties in

connection with the processing and separation of the different metals. The refinery industry therefore desires catalysts with supports that are acid resistant, especially where supports for hydroporessing 5 catalysts are concerned.

Another demand placed upon catalysts quite generally is that the catalyst should be able to retain their pore structure and their catalytically active surface under the conditions prevailing during the processes 10 in which the catalysts are used. This means, for catalytic cracking, that the cracking catalysts must be able to retain their structure and catalytically active surface at temperatures of up toward 750°C and also in the presence of water vapour. In most catalytic 15 processes, it is also required that the catalyst have a high mechanical strength to be able to withstand the strain to which it is subjected during the catalytic process.

One object of the present invention is to obviate 20 the shortcomings of known hydrocarbon processing catalysts by providing a novel type of structure for the catalyst support. Another object of the present invention is to provide a hydrocarbon processing catalyst and a support therefor having a surface area of at 25 least 75 m<sup>2</sup>/g and an average pore diameter of at least 100 Å, at least 75% of the surface area being present in pores having a diameter exceeding 100 Å. A further object of the invention is to provide a novel catalyst and a support therefor having higher mechanical, thermal 30 and hydrothermal stability than the corresponding conventional catalyst, so that it can be used in catalytic processes, such as catalytic cracking, hydro-cracking, hydroporessing, automobile exhaust emission control etc. Another object of the invention is to 35 provide a process for producing such a support or catalyst, and still another object of the invention is to provide a support or catalyst and a process

for producing such a support or catalyst which has aggregate particles in the form of a coherent three-dimensional network of mineral particles having fibrous and strip-shaped structure. Still another object of  
5 the invention is to provide, in the production of such a support or catalyst, a desired pore diameter by pretreating natural mineral particles having fibrous or strip-shaped structure. Finally, it is the object of the invention to provide a cracking catalyst of  
10 aggregate particles having the said coherent three-dimensional network of such mineral particles having fibrous or strip-shaped structure, granules of zeolite material being enclosed within said network.

Since we have found that a mineral based catalyst  
15 support is useful as a filler in e.g. polymers, a further object of the present invention is to provide such a filler having a new structure.

A filler or a support for catalytic substances according to the present invention consists of aggregate  
20 particles having a coherent three-dimensional network structure of mineral particles having fibrous or strip-shaped structure and a diameter of at least 100 Å and a mechanical, thermal and hydrothermal stability required for the contemplated use or catalytic process.

25 The support has a surface area of at least  $75 \text{ m}^2/\text{g}$  and an average pore diameter of at least 100 Å, at least 75% of the surface being present in pores having a diameter exceeding 100 Å. In the coherent three-dimensional network structure, the zeolite particles may  
30 be distributed and locked. As aluminium silicate and magnesium silicate mineral particles having fibrous or strip-shaped structure use may preferably be made of attapulgite, sepiolite and chrysotile, separately or in mixture. The characteristic features of the  
35 filler or support and the catalyst, respectively, according to the present invention will appear from the claims.

10

In the process according to the invention, the filler or support for the catalytically active substance is produced by forming a well-dispersed slurry of industrial mineral particles which have the requisite 5 particle diameter in the natural state or to which this particle diameter has been imparted by modification. Zeolite particles may, if necessary, be suspended in the said well-dispersed slurry which then either is spray-dried in order directly to form the aggregate particles, or is extruded or pelletised to form 10 such aggregate particles, or is first spray-dried to aggregate particles which are then slurried and extruded or pelletised to the desired catalyst support particles. In the production of a catalyst, a catalytic 15 substance or a precursor thereof is applied as a surface coating on the fibrous or strip-shaped particles of the support prior to or after spray-drying, extrusion or pelletisation of the support particles. The characteristic features of the process according to the 20 invention will appear from the claims.

The first step in the production of a catalyst support having the desired characteristics is to produce an extremely well-dispersed slurry of fibrous or strip-shaped industrial minerals, especially aluminium silicates or magnesium silicates, in water. In 25 the production of a cracking catalyst, it is possible simultaneously or in a separate step to suspend zeolite particles in this slurry. By "extremely well-dispersed slurries" is here meant that the mineral fibres or strips and the zeolite particles, if any, are to be 30 suspended separately in the slurry and thus preferably should form no aggregates at all. Examples of aluminium silicates having fibrous or strip-shaped structure are attapulgite and sepiolite. An example of fibrous 35 or strip-shaped magnesium silicates is chrysotile.

An example of useful zeolites employed for cracking catalysts is faujasite, i.e. zeolite Y and zeolite X,

mordenite and zeolites of the type ZSM. The zeolite content may be from low contents of, for example, 0.5% by weight up to 75% by weight, based on the finished catalyst. A useful content range is 10-75% 5 by weight, especially 25-60% by weight. The zeolite particles preferably have a particle size of 0.1-5 µm, preferably 0.5-5 µm, or 0.5-3 µm.

To make the fibrous or strip-shaped mineral particles and the zeolite particles, if any, form extremely 10 well-dispersed slurries having a high dry content, dispersing agents, such as water glass, aluminium hydroxy chloride, polyphosphates etc. are used.

One possibility of producing, in the process according to the present invention, the catalyst support 15 with a large surface area in combination with a large average pore size and high mechanical, thermal and hydrothermal stability is to spray-dry an extremely well-dispersed slurry of, for example, attapulgite dispersed in water with water glass as dispersing agent, zeolite particles also having been dispersed 20 in the slurry when a cracking catalyst is to be produced.

Another possibility of producing, in the process according to the present invention, a catalyst support 25 with a large surface area in combination with a large average pore size and high mechanical, thermal and hydrothermal stability is to form an extremely well-dispersed slurry of, for example, attapulgite and, where appropriate, zeolite particles in water by means 30 of water glass, whereupon this slurry is pelletised to support and catalyst particles, respectively.

A third possibility of producing, in the process according to the present invention, the support or 35 the catalyst with a large surface area in combination with a large average pore size and high mechanical, thermal and hydrothermal stability is first to spray-dry extremely well-dispersed slurries of, for

example, attapulgite and, where appropriate, zeolite particles in water with water glass as a dispersing agent, and then to re-slurry these spray-dried particles in water to a viscous mass which then is extruded or pelletised to form the final support and catalyst material, respectively.

The present invention also comprises the production of catalyst supports formed for mixtures of different types of fibrous or strip-shaped mineral particles.

Furthermore, the invention comprises the production of catalysts or catalyst supports which, in their network structure of fibrous or strip-shaped mineral particles, contain other incorporated particles than zeolite particles, for example particles of aluminium oxide.

Such a mixed structure of fibres and zeolite and/or other particles has a bimodal pore size distribution i.e. a first pore size distribution which is characteristic of, for example, the zeolite (e.g. about 12 Å pores having a pore opening of 7-8 Å) or of aluminium oxide (e.g. 40-100 Å) as a support for desulphurisation catalysts, and a second pore size distribution within the range 100-1000 Å which is characteristic of the support structure according to the present invention. It is also possible to give spray-dried supports according to the present invention, by modification of the surface of the fibrous or strip-shaped mineral particles included, a structure with acid seats, such that also the support proper will obtain cracking catalytic activity. For such use, it is also possible to include in the network-like structure particles of zeolite of, for example, the type H-Y or ReY.

As has been mentioned above, the fibrous or strip-shaped mineral particles may be modified prior to the production of the three-dimensional network struc-

ture. Such modification may serve to increase the fibre diameter, thereby to increase the average pore size of the resulting network structure, or may serve to deposit catalytically active substances on the surface of the mineral particles. However, catalytically active substances may be supplied also after the desire network structure has been produced by extrusion, pelletisation and/or spray-drying. The catalytically active substance may be supplied for example by im-  
5 pregnation with a precursor of the catalytic substance, such as platinum, palladium etc., which then is formed  
10 such as platinum, palladium etc., which then is formed in situ on the fibres or strips of the support.

In order positively to achieve the requisite high degree of dispersion in the slurry prior to spray-  
15 drying, extrusion or pelletisation, a dispersing agent should be used. Many conventional dispersing agents are in the form of sodium salts. If such dispersing agents are used for the production of the catalyst support by spray-drying, extrusion or pelletisation  
20 in accordance with the present invention, the resulting catalyst support will in that case contain sodium in different amounts. If sodium is detrimental to the subsequent catalytic process, the sodium content must be reduced by washing and ion exchange. It may,  
25 however, be difficult to remove all of the sodium from the catalyst support. For some purposes, e.g. catalytic cracking, it is highly important to maintain the sodium content of the final catalyst at as low a level as possible so that the requisite high hydro-  
30 thermal stability is achieved. In such cases, it is therefore necessary to use sodium-free dispersing agents, if one wants to have sodium-free catalyst supports. Examples of such sodium-free dispersing agents are aluminium hydroxy chloride, tetramethyl ammonium silicate, tetraethanol ammonium hydroxide,  
35 ammonium citrate, ammonium tartrate, ammonium glycolate etc., all of which are excellent dispersing agents

for fibrous or strip-shaped aluminium silicates and magnesium silicates, such as attapulgite, sepiolite, chrysotile etc.

If one elects, in the preparation of the slurries of said fibrous or strip-shaped mineral particles, to admix mineral, such as montmorillonite, kaolinite etc., the amounts of these substances must not exceed 50% by weight.

If kaolin is admixed to a slurry of, for example, attapulgite, the admixture of kaolin which is a cheaper material than attapulgite, implies that the spray-dried, pelletised or extruded structures will have a lower surface area and higher density, which in some cases may be disadvantageous.

The characteristics of the catalyst supports produced by spray-drying, extrusion or pelletisation of slurries of fibrous or strip-shaped mineral particles can be improved by different aftertreatments. One way of improving the mechanical strength and fixing the pore structure is to thermally treat the spray-dried particles in the temperature range 100-700°C. Another way of increasing the mechanical strength and fixing the pore structure is to coat the surface of the spray-dried, extruded or pelletised particles of the fibrous or strip-shaped mineral with silica according to prior art technique. After washing and drying, the spray-dried silica-coated particles are subjected to heat treatment in the temperature range 100-700°C.

In producing the support or catalyst, it has proved advantageous to subject the raw material, i.e. the mineral having the fibrous structure, to a pretreatment in order to modify the mineral structure. This modification is carried out as an acid treatment with an acid to remove some of the elements in the mineral structure. However, the acid treatment must be carried out for such a short time or with an acid so diluted

that the mineral will retain its basic structure.

In one embodiment of the acid treatment, the mineral can be treated with a 20% sulphuric acid solution in which the mineral is agitated for 1-3 hours at a temperature of 30-80°C. After separation of the mineral from the sulphuric acid solution, washing with deionised water is carried out, whereupon drying is effected, for example at 120°C.

An acid treatment with sulphuric acid involves that, for example, Na, K, Ca, Mg, Al and Fe are partly removed from the mineral structure. Furthermore, the removal of Al results in a change of the Si:Al ratio in the mineral structure, especially in the outer regions of the crystal complexes.

Acid treatment may also be carried out with hydrochloric acid in water in a concentration of 1:1 to 1:10.

A modification by means of weak acids results in but a slight leaching of Fe and K, and also the leaching of Al will be less strong. However, the leaching of Ca is still strong and Ca can be removed to almost 100% by leaching for 1 hour at 20°C. An increase of the leaching temperature will also increase the leaching of Al and Mg.

If attapulgite is leached with 20% sulphuric acid in the manner described above, about 10% of the originally present Al and about 20% of the originally present Mg will be removed.

Generally, it can be said that hydrochloric acid is less aggressive to the minerals than sulphuric acid. Moreover, it should be pointed out that the various minerals are affected to different degrees and in different manners depending on the structure of the minerals.

As has been mentioned above, the catalytically active material required in a hydropyrolysis or hydrogenation catalyst according to the present invention

can be supplied at different stages of the production process. Three different main processes may be distinguished, viz. 1) coating before spray-drying, 2) coating after spray-drying, and 3) coating after extrusion or pelletisation of the slurry or the re-slurried spray-dried material.

In the main process 1, the catalytically active substance is deposited on the fibrous or strip-shaped mineral particles while these are in the form of a slurry. The slurry of the particles coated with catalytically active substance are then shaped into larger particles by spray-drying, extrusion or pelletisation.

In the main process 2, the catalytically active substance is deposited on the support material after spray-drying thereof. Prior to extrusion or pelletisation, the spray-dried particles coated with catalytically active substances may, optionally, be mixed with spray-dried aluminium oxide particles which also have catalytically active substances on their surface.

In the main process 3, a support material in the form of larger aggregate particles is first produced by extrusion or pelletisation of the well-dispersed slurry of fibrous or strip-shaped mineral particles, or by first spray-drying and then re-slurrying the slurry in water prior to extrusion or pelletisation. These larger aggregate particles of fibrous or strip-shaped mineral materials are then provided with a catalytically active surface on the fibre material by depositing on this surface a catalytically active substance. Also in this instance, spray-dried aluminium oxide particles may, optionally, be admixed prior to extrusion or pelletisation.

In the above-mentioned main process 1, the catalytically active substance may be deposited in different ways on the fibrous or strip-shaped particles of the support material. One possibility of producing active hydroprocessing catalysts is to deposit on

the fibrous or strip-shaped mineral particles very small particles of catalytically active substances according to a microemulsion technique disclosed in the PCT publication WO81/02688 (PCT/SE81/00091). According to this publication, a microemulsion is first produced in which small particles of the contemplated active catalyst material, e.g. small particles of cobalt and molybdenum sulphide, are suspended. The microemulsion is then mixed with the slurry of the fibrous or strip-shaped mineral material, the said fibrous or strip-shaped mineral particles being coated with a monolayer of small particles of cobalt and molybdenum sulphide. After that, the slurry is spray-dried or extruded. Similarly, a hydrogenation catalyst can be produced by first preparing a microemulsion in which small particles of metallic platinum are suspended. Another possibility of depositing the catalytically active substance is to form first a colloidal slurry of particles, the surface of which has been coated with a catalytically active substance, in accordance with Swedish patent application 8400426-6 of January 30, 1984. This colloidal slurry is then mixed with the slurry of fibrous or strip-shaped mineral particles. In the production of hydroprocessing catalysts, it is thus possible first to produce a sol of silicic acid or aluminium silicate, the surface of which is coated with cobalt and molybdenum sulphide. Upon admixture to the slurry of fibrous or strip-shaped mineral material, the fibres of this material will obtain a monolayer of colloidal sol particles. The same technique can be used for producing a hydrogenation catalyst, the silicic acid sol, aluminium silicate or alkali aluminium silicate sol particles having metallic platinum on their surface.

Another possibility of applying catalytically active substance is by precipitation. In the production of hydroprocessing catalysts, it is thus possible

first to produce a slurry of the fibrous or strip-like mineral particles. After that, a solution of cobalt compounds and molybdenum compounds is admixed to the slurry under controlled conditions and intense agitation. In this manner, each individual fibre or strip of the fibrous or strip-shaped mineral material can be provided with a thin coating of cobalt and molybdenum compounds. If the cobalt and the molybdenum should not be in the form of sulphides, sulphidisation can be effected to convert the cobalt and the molybdenum into cobalt and molybdenum sulphide. Correspondingly, it is possible, in the production of a hydrogenation catalyst, first to prepare a slurry of the fibrous or strip-shaped mineral material and then to supply a platinum salt under controlled reducing conditions and intense agitation. In this manner, a thin layer of metallic platinum will be precipitated on the particles of the support material. Finally, spray-drying or extrusion to larger catalyst particles is effected.

Also in the above-mentioned main process 2, the catalytically active substance may be deposited in different ways on the support material. One possibility is to impregnate spray-dried particles of the fibrous or strip-like mineral material which, optionally, has been mixed with spray-dried particles of aluminium oxide, with solutions of the catalytically active substance or precursors thereof. A hydroprocessing catalyst may thus be produced by impregnating a spray-dried powder of the fibrous or strip-shaped mineral material (possibly in mixture with spray-dried aluminium oxide particles) with a solution of ammonium molybdate in water. After the water has been driven off, the spray-dried powder is impregnated with the solution of cobalt nitrate in water. After drying and calcining, cobalt and molybdenum are present as oxides on the surface of the individual fibres or strips of the support material. To produce hydrogenation catalysts,

the spray-dried powder can be impregnated correspondingly with a solution of chloroplatinic acid, whereupon the solvent is driven off and reduction to metallic platinum is effected so that the inner surfaces of  
5 the spray-dried particles are coated with metallic platinum. Also in this instance, the above-mentioned microemulsion technique may be employed for depositing particles of cobalt and molybdenum sulphide or cobalt and molybdenum hydroxide. If the particles  
10 deposited according to the microemulsion technique are in the form of oxide-hydroxides, such particles may be converted into sulphides by sulphidisation. Also for the above-mentioned main process 2, use may be made of the technique of supplying the catalytically  
15 active material by means of small colloidal particles provided on their surface with the said catalytically active material. It is thus possible to mix the spray-dried powder which may contain or may be mixed with spray-dried aluminium oxide powder, with a sol whose  
20 individual particles are provided on their surface with a coating of cobalt and molybdenum hydroxides. These hydroxides may then be converted into sulphides by sulphidisation after coating of the support material. Similarly, it is possible in the main process 2 to  
25 produce hydrogenation catalysts by first coating the individual particles of a silicic acid sol, aluminium silicate sol or an alkali aluminium silicate sol with metallic platinum, whereupon this modified sol is used for impregnating spray-dried particles of the  
30 fibrous or strip-shaped mineral particles which also in this instance may be mixed with a spray-dried powder of aluminium oxide.

Also in the above-mentioned main process 3, the shaping of the support material into active catalysts  
35 may be carried out in different ways. Thus, the support material in the main process 3 is in the form of an extrudate formed either of a slurry of fibrous or strip-like mineral particles, optionally in mixture

with spray-dried particles of aluminium oxide, or of a slurry formed of spray-dried particles of the fibrous or strip-shaped mineral material, optionally in mixture with spray-dried particles of aluminium oxide.

- One possibility in the main process 3 thus is to impregnate the extrudates with solutions of the catalytically active substances or precursors thereof. To produce hydroprocessing catalysts, it is thus possible to impregnate the extrudate with a solution of ammonium molybdate. After the water utilised as solvent has been driven off, the extrudate is impregnated with a solution of cobalt nitrate. After calcining, the cobalt and the molybdenum are present as oxides.
- By sulphidisation, the cobalt and molybdenum oxide can then be converted into the corresponding cobalt and molybdenum sulphides which are the catalytically active substances. To produce a hydrogenation catalyst, the extrudate can be impregnated with chloroplatinic acid. After the water has been driven off and after reduction, the individual particles of the extrudate are coated with platinum which is the catalytically active substance in the hydrogenation catalyst.

Also in the above-mentioned main process 3, use can be made of the microemulsion technique to apply the catalytically active substances. Thus, a hydroprocessing catalyst can be produced by impregnating the extrudate with a previously prepared microemulsion in which cobalt and molybdenum sulphide or cobalt and molybdenum oxide-hydroxide is suspended. If the particles applied according to the microemulsion technique are present as oxide-hydroxides, these can be converted into sulphides by sulphidisation. Similarly, it is possible to produce hydrogenation catalysts by utilising, in the above-mentioned manner, microemulsion technique in order to deposit on the surfaces of the support a thin layer of platinum or some other

metal from the platinum group. Also in the above-mentioned main process 3, use can be made of the technique of supplying the catalytically active substance by means of sols, the particle surfaces of which are 5 coated with the catalytically active substance. This is done in the same manner as in the main process 2, althoug coating in this case occurs on the extrudate instead of on the individual particles of fibrous or strip-shaped mineral material, optionally in mix- 10 ture with spray-dried particles of aluminium oxide.

Hydroprocessing or hydrogenation catalysts produced in accordance with the present invention are characterised by a high average pore size in combination with a high surface area. Such catalysts may be used 15 with advantage in processes in which large molecules or aggregates of molecules must be converted, such as the catalytic hydroprocessing of heavy fuel oils, in order to remove metallic impurities and heteroatoms, such as sulphur and nitrogen.

Also the cracking catalysts according to the 20 present invention are characterised by a high average pore size in combination with a large catalytically active surface area accomplished by spray-drying and/or pelletisation of a well-dispersed slurry of zeolite 25 particles and fibrous or strip-shaped aluminium silicate or magnesium silicate minerals. The surfaces of the fibrous or strip-shaped particles included in the catalyst may be provided with a surface of aluminium silicate or alkali aluminium silicate converted into 30 catalytically active form by ion exchange with hydrogen ions or ions of rare earth metals.

The cracking catalyst production according to the present invention may also be carried out in accordance with three main processes, viz.

35 1. A well-dispersed slurry is formed of zeolite particles and particles of fibrous or strip-shaped aluminium or magnesium silicates and is then

5 spray-dried. If the zeolite is not in the desired form for catalytic cracking, the zeolite may be converted into such form by subjecting the spray-dried particles to a succession of ion exchange steps, for example ammonium ion exchange and ion exchange with rare earth metals.

10 2. Particles of fibrous or strip-shaped aluminium or magnesium silicates in a well-dispersed slurry are given a catalytically active surface or a precursor thereof.

15 10 The slurry of zeolite and fibrous or strip-shaped particles is then spray-dried to a structure which is characterised by the above-mentioned high average pore size in combination with a large surface area. If the zeolite particles or the fibrous or strip-shaped particles are not in the final catalytic form, they can be converted thereto by a succession of ion exchange steps, such as an ammonium ion exchange and ion exchange with rare earth metals.

20 20 3. A slurry of zeolite particles and fibrous or strip-shaped aluminium silicate magnesium silicate mineral is spray-dried to particles of the above-mentioned structure having a high average pore size in combination with a large surface area. After that the spray-dried particles are impregnated with a catalytically active substance or a precursor thereof. If the coating on the fibrous or strip-shaped particles consists of such a precursor or if the zeolite is not in the final catalytic form, the precursor and the zeolite, respectively, can be converted into this catalytically active form by a series of ion exchange steps with ammonium ions and ions of rare earth metals.

35 One way of producing a cracking catalyst according the main process 1 of the present invention is

to prepare a slurry of zeolite, for example zeolite Y in sodium form, and fibrous or strip-shaped aluminium or magnesium silicates. The slurry is spray-dried, and the spray-dried particles are shaped into 5 an active cracking catalyst by ion exchange. By ammonium ion exchange, washing, drying and calcining, a cracking catalyst in hydrogen form is produced. By ion exchange of spray-dried particles, first with ammonium and then with ions of rare earth metals, a catalyst in 10 rare earth form is produced. A particularly interesting way of producing a catalyst according to the main process 1 is to proceed from an acid-leached attapulgite and zeolite of the type ultrastable hydrogen Y. A well-dispersed slurry of the attapulgite and this 15 zeolite in water is formed with aluminium hydroxy chloride as dispersing agent, followed by spray-drying and calcining at 500-600°C, whereby a catalyst is obtained which has a very low sodium content and, thus, a very high hydrothermal stability.

One way of producing the cracking catalysts according to the main process 2 of the present invention 20 is to coat in a slurry the particles or fibrous or strip-shaped aluminium or magnesium silicates with a monolayer of small sol particles. The sol particles consist of aluminium silicate, preferably in ammonium 25 form, or alkali aluminium silicate. The sol particles may also consist of silicic acid, but then the particle surface must be modified by means of aluminate or alkali aluminate to an aluminium silicate and alkali 30 aluminium silicate, respectively, which is converted into the ammonium form. If the surface area of the fibrous or strip-shaped aluminium or magnesium silicate is known, one can calculate the amount of sol that must be supplied to the slurry of fibrous or 35 strip-shaped aluminium or magnesium silicate particles in order to coat each particle with a monolayer of sol particles. To this slurry are added particles

of zeolite Y, preferably in the ammonium form, the zeolite being supplied in the form of a powder or slurry. The slurry of the zeolite particles and the coated fibrous or strip-shaped particles is spray-dried to particles having an average particle size of about 5 70 µm. If the zeolite or the surface coating of the fibrous or strip-shaped particles is present in the ammonium form, this can be converted into the hydrogen form by calcining at about 500°C, whereby ammonia 10 is expelled and the hydrogen form of the zeolite and the aluminium silicate is established. If zeolite Y and the surface coating of the fibrous or strip-shaped particles are in the ammonium form, ammonium ions 15 may be replaced by ions of rare earth metals by slurrying the spray-dried particles and effecting ion exchange with a solution of, for example, chlorides of rare earth metals according to prior art technique. If zeolite Y and the surface coating of the fibrous or spray-dried particles are in the sodium form, this 20 is converted into catalytically active form by slurring the spray-dried particles in a solution of ammonium sulphate. After filtration and washing, the spray-dried particles in the ammonium form are slurried in a solution of chlorides of rare earth metals. After filtration 25 and drying, the catalyst is obtained in the rare earth form.

Another way of producing an efficient cracking catalyst according to the main process 2 is to coat the fibrous or strip-shaped aluminium silicate or 30 magnesium silicate particles with a homogeneous layer of aluminium silicate. Solutions of alkali aluminate and alkali silicate or a solution of alkali aluminium silicate are then added simultaneously at a carefully controlled rate and under intense agitation to the 35 slurry of the fibrous or strip-shaped particles, whereby each particle in the slurry is coated with an alkali aluminium silicate layer, the thickness of which may

be varied from a few Ångström to several hundred Ångström. The slurry of the particles thus coated is mixed with particles of zeolite Nay in the form of a powder or a slurry and is spray-dried to particles having an 5 average particle size of 70 µm. Alkali ions, such as sodium or potassium ions, are replaced by ammonium ions in that the spray-dried particles are slurried in a solution of ammonium sulphate. After filtration and washing, the ammonium form may be converted into 10 the hydrogen form by calcining of the spray-dried particles at 500°C.

If it is desired to convert the catalyst into a form containing ions of rare earth metals, the filtrate of the spray-dried particles which are present 15 in the ammonium form, is slurried in a solution of chlorides of rare earth metals. A finished catalyst is obtained by filtration, washing and drying of the spray-dried particles.

One way of producing a cracking catalyst according 20 to the main process 3 of the present invention is to spray-dry slurry of zeolite particles, such as zeolite Y in the ammonium form, and fibrous or strip-shaped aluminium or magnesium silicate to particles having an average particle size of 70 µm. The surface 25 of the spray-dried fibrous or strip-shaped particles is coated with a monolayer of aluminium silicate particles or silicic acid particles, the surface of which has been modified with aluminium to aluminium silicate. The particles of aluminium silicate preferably should 30 be in the ammonium form. After coating of the spray-dried particles with a monolayer of small sol particles of ammonium aluminium silicate, ammonium can be driven off by calcining at 500°C, the zeolite being converted into the hydrogen form and a surface of aluminium silicate in the hydrogen form being established. After 35 the surface of the spray-dried particles has been coated with small sol particles of aluminium silicate

in the ammonium form, ammonium may be replaced by ions of rare earth metals by ion exchange with a solution of chlorides of rare earth metals.

The cracking catalysts according to the present invention are characterised by a high average pore size in combination with a large surface area. These catalysts may be used with advantage for cracking heavy oils, especially heavy residual oils, whereby several of the problems encountered in the cracking of heavy oils in present-day refineries are avoided.

Thus, large molecules and aggregates of molecules present in the heavy oils will have easy access to the catalytically active surface of fibrous or strip-shaped aluminium or magnesium silicates, while fragments of large molecules or smaller molecules will have easy access to the catalytically active surface of the zeolite for cracking. The driving-off, the "stripping", of products from the catalyst preparatory to regeneration of the catalyst will also be more efficient so that no products or large molecules are carried along to the regenerator to be burned therein and to cause undesired high temperatures in the regenerator.

The extruded, pelletised or spray-dried supports according to the present invention may be used after impregnation with precious metals, such as platinum, palladium etc., as oxidation catalysts in, for example, automobile exhaust emission control.

As has been mentioned above, the extruded, pelletised or spray-dried supports according to the invention may be used, after impregnation with catalytically active substances, such as cobalt, molybdenum, nickel, tungsten etc., also as hydroprocessing catalysts.

In the following, a number Examples are given to illustrate the invention in more detail. In these Examples, attapulgite having the trade name "ATTAGEL 50" and purchased from Engelhart Minerals, was utilised.

This attapulgite contains 68% SiO<sub>2</sub>, 12% Al<sub>2</sub>O<sub>3</sub> and 10.5% MgO.

In the Examples, soda water glass or sodium silicate solution from EKA Kemi AB was used. The ratio 5 of SiO<sub>2</sub> to Na<sub>2</sub>O was in this instance 3.3:1, the SiO<sub>2</sub> content being 26.6% and the density 1350 kg/m<sup>3</sup>.

The aluminium hydroxy chloride employed had the formula Al<sub>2</sub>(OH)<sub>5</sub>Cl·3H<sub>2</sub>O and was purchased from Hoechst under the trade name "KLORHYDROL ACH".

10 The spray drier utilised for the tests was a pilot spray drier from Niro A/S, Denmark, having a diameter of 9 feet (2.75 m). The spray drier had a rotating spreader wheel, variable air flow, variable speed of the spreader wheel, variable input and output temperatures, and variable inflow. Typical running 15 conditions during the spray-drying of the slurries in the following Examples where:

	Spreader wheel speed	13500 r/m
	Temperature of inlet air	450°C
20	Temperature of outlet gas	150°C
	The moisture content of the spray-dried particles varied between	10 and 30%
25	For determining the dispersion degree of molybdenum, cobalt and platinum, use was made of a measuring apparatus "KEMISORB 2800" from Micromeritics. The relationship between the dispersion degree and catalytic activity is described in a paper entitled "A Study of Relationships between Pore Size Distribution, Hydrogen Chemisorption, and Activity of Hydrodesulphurization Catalysts", Journal of Catalysis, Vol. 72, pp. 266-273,	
30	Catalysts", Journal of Catalysis, Vol. 72, pp. 266-273, 1981. The microemulsion technique for the production of fine-grained platinum and other precious metals is described in the PCT publication WO81/02688 (PCT/SE81/00091).	

35 Pore sizes were determined by means of an apparatus "DIGISORB 2600" from Micromeritics.

If a catalyst or catalyst support according to the invention is produced by extrusion moulding, use may be made of conventional extrusion moulding machines for use in catalyst production or in the ceramic industry. To obtain satisfactory results, it has been found to be extremely important to maintain a correct moisture content in the mass to be extruded, and in this respect it has been found that, for the object of this invention, the best results are obtained at 5 a moisture content of 30-50%. In those cases where extrusion moulding has been used in the following Examples, a moisture content within this range has been used. The diameter of the extrudates has been selected within the range 0.8-3.2 mm. After extrusion 10 moulding, the extrudates are dried, and in the Examples this has been done by linearly increasing the temperature of the extrudate from room temperature up to 200°C at a temperature increase rate of 85°C/hour, sometimes 100°C/hour, whereupon the extrudates have 15 been maintained at 200°C for 2 hours. After heating, 20 the extrudates were allowed to cool to room temperature in stationary air.

In the following Examples 53, 54 and 61, the fibrous clay minerals are pretreated by an acid treatment before the catalyst support is produced. This 25 acid treatment is carried out in the following manner:

- A. 35 g of fibrous material are mixed with 500 ml of 20% sulphuric acid ( $H_2SO_4$ ) and agitated at 20-80°C for 1-3 hours.
- B. The mineral is separated from the solution.
- C. The mineral is washed with deionised water.
- D. The washed mineral is dried at 120°C.

During the acid treatment, the fibrous structure (basic structure) on the mineral is maintained, which 35 can be confirmed by X-ray analysis. As a result of the acid treatment, some elements were removed from the mineral structure. In respect of attapulgite,

about 20% of the aluminium and 20% of the magnesium normally present in the mineral were leached out.

EXAMPLE 1

Production of a support

- 5 To form a well-dispersed slurry, 2.85 kg "ATTAGEL 50" are added to 10 litres of water containing water glass in a ratio of 3.3:1. The water glass content of the slurry is made to correspond to 3.5 g SiO<sub>2</sub> from the water glass per 100 g of dry attapulgite.
- 10 The attapulgite is added under intense agitation. The final attapulgite content is 22% by weight of dry attapulgite. The attapulgite slurry is then spray-dried under the above-mentioned conditions. Spray-dried particles have an average pore size of 426 Å and a
- 15 surface area of 109 m<sup>2</sup>/g. 93% of the surface area are in pores having a diameter exceeding 100 Å.

EXAMPLE 2

Production of a support

- Example 1 is repeated, but after spray-drying 20 the spray-dried particles are calcined at 500°C for 1 hour. After calcining, the spray-dried particles have an average pore size of 362 Å and a surface area of 111 m<sup>2</sup>/g. 87% of the surface area are in pores exceeding 100 Å.

25

EXAMPLE 3

Production of a carrier

- Example 1 is repeated, but the spray-dried particles are aged at 750°C in an atmosphere of 100% relative humidity for 18 hours. After aging, the spray-dried particles have an average pore size of 465 Å and a surface area of 101 m<sup>2</sup>/g. 91% of the surface area are in pores having a diameter exceeding 100 Å.

EXAMPLE 4

Production of a support

- 35 Attapulgite in an amount corresponding to 1.81 kg of dry attapulgite is added to 10 litres of water containing "KLORHYDROL ACH". The content of "KLORHYDROL

30

ACH" in the well-dispersed slurry corresponds to 15 g Al<sub>2</sub>O<sub>3</sub>, based on 100 g of dry attapulgite. The attapulgite is added under intense agitation. The slurry of attapulgite which has been dispersed with "KLOR-HYDROL ACH", is spray-dried. The spray-dried particles have an average pore size of 410 Å and a surface area of 125 m<sup>2</sup>/g. 85% of the surface area are in pores exceeding 100 Å.

EXAMPLE 5

10           Production of a support

Example 1 is repeated, but the spray-dried particles are calcined at 750°C for 1 hour. After calcining, the spray-dried particles have an average pore size of 380 Å and a surface area of 91 m<sup>2</sup>/g. 80% of the surface area are in pores having a diameter exceeding 100 Å.

EXAMPLE 6

Production of a support

Example 1 is repeated with a well-dispersed slurry of attapulgite which is dispersed with aluminium citrate. The same result is obtained.

EXAMPLE 7

Production of a support

A well-dispersed slurry of sepiolite in water is dispersed with water glass and spray-dried. A three-dimensional network structure is obtained in the spray-dried particles.

EXAMPLE 8

Production of a support

30           A well-dispersed slurry of attapulgite with water glass is extruded to support particles having a three-dimensional network structure.

EXAMPLE 9

Production of a support

35           A well-dispersed slurry of attapulgite in water is dispersed by means of water glass and spray-dried. The spray-dried particles are slurried in water to

31

a viscous slurry which is extruded to catalyst support particles.

EXAMPLE 10

Production of a support

5 A well-dispersed slurry of attapulgite is dispersed with water glass and spray-dried. The spray-dried particles are coated with silica. After the coating with silica, the spray-dried particles are heated at 500°C for 1 hour.

EXAMPLE 11

Production of a support

A well-dispersed slurry containing 75% attapulgite and 25% kaolin is dispersed with water glass and spray-dried. The spray-dried particles have a structure in the form of a three-dimensional network of attapulgite fibres, and the kaolin particles are mechanically retained in the three-dimensional network.

EXAMPLE 12

Production of a support

20 A well-dispersed slurry of attapulgite in water and water glass as dispersing agent is formed. The fibre surfaces of the slurried particles are coated with a 200 Å thick layer of aluminium silicate, followed by spray-drying. Support particles of aluminium silicate-coated attapulgite fibres in a three-dimensional network structure are obtained.

EXAMPLE 13

Production of a support

30 A well-dispersed slurry of 50% attapulgite and 50% chrysotile in water is formed, water glass being used as dispersing agent. During spray-drying of the slurry, support particles are formed which have a three-dimensional network with pores corresponding approximately to the diameter of the attapulgite and the chrysotile.

EXAMPLE 14Production of hydroprocessing catalyst

Attapulgite in an amount corresponding to 1.82 kg of dry attapulgite is added to 10 litres of water containing, as a dispersing agent, aluminium hydroxy chloride in an amount corresponding to 16 g  $\text{Al}_2\text{O}_3$  per 100 g of dry attapulgite. The attapulgite is added under intense agitation. When all attapulgite has been added, the well-dispersed slurry contains 15% by weight of attapulgite, calculated as dry attapulgite. The resulting slurry is spray-dried. 100 g of the spray-dried attapulgite are slowly heated to 540°C for 3 hours and then calcined at 540°C for 16 hours. 10 g of the calcined attapulgite are then impregnated with a solution of 1.06 g ammonium molybdate  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$  in 13.77 g of water. Before the ammonium molybdate is added to the water, the ammonium molybdate is moistened with 0.47 ml ammonium hydroxide consisting of 25% ammonia in water. The ammonium molybdate-impregnated attapulgite is dried in an oven for 8 hours at 120°C. The attapulgite is agitated every 10 minutes during the first hour of drying. After drying, the attapulgite is impregnated with a solution of 0.58 g of cobalt nitrate  $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$  in 15.27 g of water. The impregnated attapulgite is dried for 8 hours at 120°C. The catalyst is agitated every 10 minutes during the first hour of drying. The attapulgite impregnated with cobalt and molybdenum salts is slowly heated to 540°C and calcined at this temperature for 10 hours. The spray-dried attapulgite impregnated with cobalt and molybdenum salts has an average pore size of 360 Å and a surface area of 85  $\text{m}^2/\text{g}$ . 76% of the surface area are in pores exceeding 100 Å. The dispersion degree of the molybdenum is 89%. As a comparison, it may be mentioned that aluminium oxide ("PURALS" from Condea) impregnated with

cobalt and molybdenum in the same manner as the attapulgite above, will have an average pore size of 60 Å and a surface area of  $240 \text{ m}^2/\text{g}$ . 5% of the surface area are in pores exceeding 100 Å. The dispersion degree of the molybdenum is in this case 31%.

5 The attapulgite catalyst produced in accordance with this Example and impregnated with molybdenum and cobalt may be used as a hydroprocessing catalyst.

#### EXAMPLE 15

##### Production of a hydrogenation catalyst

10 2.85 kg "ATTAGEL 50" are added to 10 litres of water containing water glass in a ratio of 3.3:1. The water glass content in the slurry is made to correspond to 3.5 g  $\text{SiO}_2$  from the water glass per 100 g of dry attapulgite. The attapulgite is added under intense agitation. The final attapulgite content is 22% by weight of dry attapulgite. To the well-dispersed attapulgite slurry silicic acid salt particles are admixed whose surface has previously been coated with 15 platinum. The attapulgite slurry thus obtained is then spray-dried under the above-mentioned conditions. Spray-dried particles have an average pore size of 426 Å and a surface area of  $109 \text{ m}^2/\text{g}$ . 93% of the surface area are in pores having a diameter exceeding 20 100 Å.

25 If the spray-dried particles after spray-drying are calcined at  $500^\circ\text{C}$  for 1 hour, they will have, after calcining, an average pore size of 362 Å and a surface area of  $111 \text{ m}^2/\text{g}$ . 87% of the surface area are in pores exceeding 100 Å.

30 If, on the other hand, the spray-dried particles are aged at  $750^\circ\text{C}$  in an atmosphere of 100% relative humidity for 18 hours, the spray-dried particles after aging will have an average pore size of 465 Å and a 35 surface area of  $101 \text{ m}^2/\text{g}$ . 91% of the surface area are in pores having a diameter exceeding 100 Å. The particles may be used as a hydrogenation catalyst.

EXAMPLE 16Production of a hydroprocessing catalyst

Attapulgite in an amount corresponding to 1.81 kg of dry attapulgite is added to 10 litres of water containing "KLORHYDROL ACH". The content of "KLORHYDROL ACH" in the well-dispersed slurry corresponds to 15 g Al<sub>2</sub>O<sub>3</sub>, based on 100 g of dry attapulgite. The attapulgite is added under intense agitation. An aluminium silicate sol whose surface is coated with cobalt and molybdenum oxide-hydroxide is admixed to the attapulgite slurry which is then spray-dried. The spray-dried particles have an average pore size of 410 Å and a surface area of 125 m<sup>2</sup>/g. 85% of the surface area are in pores exceeding 100 Å. The particles may be used a hydroprocessing catalyst.

EXAMPLE 17Production of a hydrogenation catalyst

A well-dispersed slurry of attapulgite is prepared and spray-dried in accordance with Example 14. Conventional coating of the spray-dried material with platinum is carried out, whereupon the material is extruded. The resulting extrudate may be used as a hydrogenation catalyst.

EXAMPLE 18Production of a hydroprocessing catalyst

A well-dispersed slurry of attapulgite is prepared and spray-dried in accordance with Example 14, and the spray-dried material is coated in conventional manner with cobalt and molybdenum, followed by extrusion and sulphidisation. However, the sulphidisation may be performed in situ in the catalytic reactor. The resulting extrudate may be used as a hydroprocessing catalyst.

EXAMPLE 19Production of a hydroprocessing catalyst

A well-dispersed slurry of attapulgite is prepared and spray-dried in accordance with Example 14. The

spray-dried attapulgite is coated with aluminium oxide sol, the sol particle surfaces of which are coated with oxide-hydroxides of molybdenum and nickel. After extrusion and sulphidisation, the resulting extrudate 5 may be used a hydroprocessing catalyst.

EXAMPLE 20

Production of a hydroprocessing catalyst

A well-dispersed slurry of attapulgite is prepared and spray-dried in accordance with Example 14. The 10 spray-dried attapulgite is mixed with spray-dried aluminium oxide. Spray-dried attapulgite and aluminium oxide are coated in conventional manner with molybdenum and cobalt. After extrusion and sulphidisation the resulting material may be used as a hydroprocessing 15 catalyst.

EXAMPLE 21

Production of a hydroprocessing catalyst

A well-dispersed slurry of attapulgite is prepared and spray-dried in accordance with Example 14. The 20 spray-dried attapulgite is mixed with the spray-dried aluminium oxide and coated with sulphides of molybdenum and nickel according to microemulsion technique. After extrusion, the resulting material may be used as a hydroprocessing catalyst.

EXAMPLE 22

Production of a hydroprocessing catalyst

A well-dispersed slurry of attapulgite is prepared and spray-dried in accordance with Example 14 and mixed with the spray-dried aluminium oxide. Spray-dried 30 attapulgite and aluminium oxide are coated with aluminium oxide sol whose sol particle surfaces are coated with oxide-hydroxides of tungsten and nickel. After extrusion and sulphidisation, the resulting material may be used as a hydroprocessing catalyst.

EXAMPLE 23

Production of a hydroprocessing catalyst

A well-dispersed slurry of chrysotile is spray-dried. The spray-dried chrysotile is coated with alu-

minium oxide sol whose sol particle surfaces are coated with oxide-hydroxides of molybdenum and cobalt. After extrusion and sulphidisation, the resulting material may be used as a hydroprocessing catalyst.

5

EXAMPLE 24Production of a hydroprocessing catalyst

A well-dispersed slurry of attapulgite and montmorillonite is prepared and spray-dried. Spray-dried attapulgite and montmorillonite are coated in conventional manner with tungsten and cobalt. After extrusion and sulphidisation, the resulting material may be used a hydroprocessing catalyst.

10

EXAMPLE 25Production of a hydroprocessing catalyst

15 A well-dispersed slurry of attapulgite and chrysotile is prepared and spray-dried. Spray-dried attapulgite and chrysotile are coated in conventional manner with molybdenum and nickel. After extrusion and sulphidisation, the resulting material may be used as a hydroprocessing catalyst.

20

EXAMPLE 26Production of a hydrogenation catalyst

An extrudate of attapulgite and aluminium oxide is formed from a well-dispersed slurry and coated 25 in conventional manner with platinum. The resulting material may be used as a hydrogenation catalyst.

25

EXAMPLE 27Production of a hydroprocessing catalyst

An extrudate of attapulgite and aluminium oxide 30 is formed from a well-dispersed slurry. This well-dispersed slurry is formed by mixing an aqueous slurry of 500 g attapulgite with such an amount of aluminium oxide that the dry content of the slurry will be above 30% and the aluminium oxide content 33%, based on 35 the dry weight of the slurry. The extrudate is then coated in conventional manner with cobalt and

37

molybdenum. After sulphidisation, the resulting material may be used as a hydroprocessing catalyst.

EXAMPLE 28

Production of a hydroprocessing catalyst

5 An extrudate of attapulgite and aluminium oxide is formed from a well-dispersed slurry and coated with aluminium oxide sol whose surface is coated with molybdenum and nickel. After sulphidisation, the resulting material may be used as a hydroprocessing catalyst.

EXAMPLE 29

Production of a hydroprocessing catalyst

10 Attapulgite ("ATTAGEL 50") in an amount corresponding to 0.50 kg of dry attapulgite is added to 1.6 litre of water which, as a dispersing agent, contains water 15 glass in an amount corresponding to 3.0 g SiO<sub>2</sub> per 100 g of dry attapulgite. The attapulgite is added under intense agitation in a Z-shaped blade kneader. When all attapulgite has been added, the slurry contains 30% by weight of attapulgite, calculated as dry atta- 20 pulgite. The resulting mass is extruded in the above- mentioned manner to extrudates having a diameter of 1.6 mm and a length of 3-5 mm. The finished extrudates are slowly heated to 200°C during 2 hours and then held at 200°C for a further 2 hours for drying.

25 100 g of the dried extrudate are then slowly heated to 540°C during 3 hours and then calcined at 540°C during a further 2 hours.

30 100 g of the calcined attapulgite extrudate are impregnated with cobalt and molybdenum in the manner stated in Example 14. The attapulgite extrudate impreg- nated with cobalt and molybdenum salts has an average pore size of 360 Å and a surface area of 108 m<sup>2</sup>/g, 75% of the surface area being in pores exceeding 100 Å.

35 After sulphidisation, the resulting material may be used as a hydroprocessing catalyst.

EXAMPLE 30Production of a hydroprocessing catalyst

An extrudate of spray-dried attapulgite is formed from a well-dispersed slurry and coated with particles 5 of molybdenum sulphide and nickel sulphide prepared by microemulsion technique. The resulting material may be used as a hydroprocessing catalyst.

EXAMPLE 31Production of a hydroprocessing catalyst

10 An extrudate of spray-dried attapulgite is formed from a well-dispersed slurry and coated with aluminium oxide sol whose sol particle surfaces are coated with oxide-hydroxides of tungsten and nickel. After sulphidisation, the resulting material may be used as a 15 hydroprocessing catalyst.

EXAMPLE 32Production of a hydroprocessing catalyst

An extrudate of spray-dried chrysotile is formed from a well-dispersed slurry and coated with aluminium 20 oxide sol, the sol particle surfaces of which are coated with oxide-hydroxides of molybdenum and cobalt. After sulphidisation, the resulting material may be used as a hydroprocessing catalyst.

EXAMPLE 33Production of a hydroprocessing catalyst

An extrudate of slurries of attapulgite and montmorillonite is formed from a well-dispersed slurry and coated in conventional manner with tungsten and cobalt. After sulphidisation, the resulting material 30 may be used as a hydroprocessing catalyst.

EXAMPLE 34Production of a hydroprocessing catalyst

An extrudate of slurries of attipulgite and chrysotile is coated in conventional manner with molybdenum 35 and nickel. After sulphidisation, the resulting material may be used as a hydroprocessing catalyst.

EXAMPLE 35Production of a hydrogenation catalyst

Attapulgite in an amount corresponding to 1.82 kg of dry attapulgite is added to 10 litres of water containing "KLORHYDROL ACH" as a dispersing agent in an amount corresponding to 16 g Al<sub>2</sub>O<sub>3</sub> per 100 g of dry attapulgite. The attapulgite is added under intense agitation. After the attapulgite has been added, the slurry contains 15% by weight of attapulgite, calculated as dry attapulgite. The slurry of attapulgite in water is spray-dried. 100 g of spray-dried attapulgite are slowly heated to 540°C for 3 hours and then calcined at 540°C for 16 hours. 10 g of the calcined attapulgite are impregnated with a suspension of platinum particles in a microemulsion of heptane. The platinum particles in the microemulsion are of the order 25 Å. The attapulgite particles are impregnated with a platinum content of 1%. After the solvent heptane has been driven off, and after drying, the spray-dried attapulgite is calcined at 600°C for 8 hours. The calcined spray-dried particles have an average pore size of 400 Å and a surface area of 95 m<sup>2</sup>/g.

If aluminium oxide ("PURAL SB" from Condea) is impregnated with 1% platinum according to conventional technique, the resulting product will have an average pore size of 60 Å and a surface area of 240 m<sup>2</sup>/g.

EXAMPLE 36Production of a cracking catalyst

2.85 kg "ATTAGEL 50" are added to 10 litres of water containing water glass in a ratio of 3.3:1. The water glass content in the slurry is made to correspond to 3.5 g SiO<sub>2</sub> from the water glass per 100 g of dry attapulgite. The attapulgite is added under intense agitation. The final attapulgite content is 25% by weight of dry attapulgite. The attapulgite in the well-dispersed slurry is coated with particles of a sol of ammonium aluminium silicate. The attapulgite slurry is then spray-dried under the above-mentioned

conditions, whereupon the spray-dried particles are calcined at 500°C for 1 hour, whereby the hydrogen form of the catalyst is obtained. After calcining, the spray-dried particles have an average pore size of 362 Å and a surface area of 111 m<sup>2</sup>/g. 87% of the surface area are in pores exceeding 100 Å.

EXAMPLE 37

Production of a cracking catalyst

Example 36 is repeated, but the spray-dried particles are aged at 750°C in an atmosphere of 100% relative humidity for 18 hours. After aging, the spray-dried particles have an average pore size of 465 Å and surface area of 101 m<sup>2</sup>/g. 91% of the surface area are in pores having a diameter exceeding 100 Å.

EXAMPLE 38

Production of a cracking catalyst

Example 36 is repeated, but the spray-dried particles are subjected to ion exchange with rare earth metals, followed by calcining at 750°C for 1 hour. After calcining, the spray-dried particles have an average pore size of 380 Å and a surface area of 91 m<sup>2</sup>/g. 80% of the surface area are in pores having a diameter exceeding 100 Å.

EXAMPLE 39

Production of a cracking catalyst

Example 36 is repeated, but sepiolite is used instead of attapulgite. Equivalent results are obtained.

EXAMPLE 40

Production of a cracking catalyst

Attapulgite in an amount corresponding to 263 g of dry attapulgite is added to an aqueous solution of water glass in a ratio of 3.3:1. The water glass content corresponds to 4% SiO<sub>2</sub>, based upon dry attapulgite. The attapulgite is added under intense agitation. When all attapulgite has been added to the slurry, the well-dispersed slurry has a dry content correspond-

ing to 20% of dry attapulgite. 1 litre of a solution of potassium aluminium silicate is prepared by mixing 56% by volume of potassium silicate which is in the ratio of 2:1 and which is 3-molar with regard to  $\text{SiO}_2$ ,  
5 with 25% by volume of 2-molar potassium aluminate and 19% by volume of water. To 1 litre of attapulgite slurry, 840 ml of the solution of potassium aluminium silicate are added for 1 hour. The temperature of the slurry is maintained at 80-85°C, and the pH of  
10 the slurry at 10-11.5 by the addition of acetic acid. In this manner, the attapulgite particles are coated with a homogeneous layer of aluminium silicate. When the addition of the potassium aluminium silicate is finished, the slurry is spray-dried. The spray-dried  
15 attapulgite is slurried in water and ion exchanged with ammonium ions by adding ammonium sulphate to the slurry at pH 4.5 and a temperature of 80°C. The spray-dried particles are filtered, and the ion exchange procedure is repeated twice. After the last ion exchange  
20 step, the spray-dried particles are filtered and washed. The spray-dried particles are then aged for 18 hours at 750°C and in 100% water vapour. The catalytic activity of the aged aluminium silicate-coated attapulgite is measured with a Micro Activity Testing apparatus  
25 (MAT testing is a technique described in literature). The test gave a yield of 50%, which should be compared to the yield obtained with an equilibrium catalyst in a commercial cracking plant. The selectivity of gasoline and diesel is excellent. The yield of gas  
30 and carbon is low.

EXAMPLE 41

Production of a cracking catalyst

A well-dispersed slurry of attapulgite is prepared and spray-dried to particles having an average pore size of 70  $\mu\text{m}$ . The surface of the spray-dried particles  
35 is coated with a layer of sol particles of aluminium silicate in the ammonium form.

42

EXAMPLE 42Production of a cracking catalyst

Example 41 is repeated, but the ammonium form of the aluminium silicate is converted into RE form.

EXAMPLE 43Production of a cracking catalyst

Example 41 is repeated, but a mixture of chrysotile and attapulgite is used as support material.

EXAMPLE 44Production of a cracking catalyst

Example 38 is repeated, but instead of attapulgite a mixture of 70% attapulgite and 30% bentonite is used.

EXAMPLE 45Production of a cracking catalyst

A well-dispersed slurry is prepared from zeolite NaY and attapulgite, utilising water glass as dispersing agent. The slurry is spray-dried, and the spray-dried particles are then subjected to ammonium ion exchange and then to ion exchange with ions of rare earth metals.

EXAMPLE 46Production of a cracking catalyst

A well-dispersed slurry is prepared from attapulgite and zeolite RE-Y, using aluminium hydroxychloride as dispersing agent. The slurry is spray-dried to particles which are calcined at 600°C.

EXAMPLE 47Production of a cracking catalyst

Example 46 is repeated, but instead of zeolite RE-Y the highly stable zeolite US-Y is used.

EXAMPLE 48Production of a cracking catalyst

A well-dispersed slurry is prepared from attapulgite, kaolin and zeolite NH<sub>3</sub>-Y, use being made of aluminium hydroxychloride as dispersing agent. The slurry is spray-dried, and the spray-dried particles

are subjected to ion exchange with ions of rare earth metals.

EXAMPLE 49

Production of a cracking catalyst

5 Attapulgite is added to an aqueous solution of chloroaluminium hydroxide under intense agitation. When all attapulgite has been added to the slurry, a sodium aluminium silicate sol is added, such that the attapulgite fibres are provided with a monolayer 10 of sol particles. To this well-dispersed slurry the zeolite NA-Y is then added. The resulting slurry of zeolite NA-Y and attapulgite is spray-dried, and the resulting particles are first subjected to ammonium ion exchange and then to ion exchange with ions of 15 rare earth metals.

EXAMPLE 50

Production of a cracking catalyst

Example 49 is repeated, but instead of attapulgite chrysotile is used.

EXAMPLE 51

Production of a cracking catalyst

Example 49 is repeated, but instead of zeolite NaY use is made of zeolite NH<sub>3</sub>-Y, the ammonium ion exchange being omitted.

EXAMPLE 52

Production of a cracking catalyst

Attapulgite is dispersed under intense agitation 25 in an aqueous solution of aluminium hydroxychloride, whereupon an ammonium aluminium silicate sol is added 30 for coating the surface of the attapulgite fibres with a monolayer of sol particles. To the resulting well-dispersed slurry a well-dispersed slurry of the zeolite US-Y is added under intense agitation. After 35 that, spray-drying is effected to particles which finally are calcined at 500°C.

EXAMPLE 53Production of a support material having high crushing strength

Attapulgite ("ATTAGEL 50") in an amount correspond-  
5 ing to 1.82 kg of dry attapulgite is added to 10 litres  
of water which, as a dispersing agent, contains alumi-  
nium hydroxy chloride in an amount corresponding to  
16 g Al<sub>2</sub>O<sub>3</sub> per 100 g of dry attapulgite.

10 The attapulgite is added under intense agitation  
to form a well-dispersed slurry. When all attapulgite  
has been added, the slurry contains 15% by weight  
of attapulgite, calculated as dry attapulgite. The  
resulting slurry is spray-dried.

15 200 g of spray-dried attapulgite are mixed in  
the dry state with 100 g attapulgite which has not  
been sprayed. This attapulgite mixture is added under  
intense agitation in a 2-blade kneader to 1.2 litre  
of water which, as a dispersing agent and binder,  
contains 3 g SiO<sub>2</sub> per 100 g of attapulgite that has  
20 not been spray-dried. When all attapulgite has been  
added, the well-dispersed mass contains 29% weight  
of dry material.

When the mass thus produced is extruded in the  
above-mentioned manner to an extrudate having the  
25 diameter 0.8-3.2 mm, the extrudate, after drying at  
200°C and calcining at 540°C in the manner stated  
in Example 29, has a BET surface area of 130 m<sup>2</sup>/g  
and an average pore size of 380 Å. This extrudate  
has high crushing strength and can be used as a sup-  
30 port for catalyst material. The catalyst material  
can be supplied in the manner previously mentioned.

EXAMPLE 54Production of a catalyst support of attapulgite  
and aluminium oxide

35 Attapulgite ("ATTAGEL 50") is mixed with water  
and a dispersing agent in accordance with Example 53  
and is spray-dried.

500 g (calculated as dry attapulgite) of the spray-dried attapulgite are mixed with 88 g aluminium oxide ("PURAL SB"). This dry mixture is added under intense agitation in a Z-shaped blade kneader to 1.3 litre 5 of water to form a mass containing 30% by weight of dry material. This mass is extruded in the manner mentioned above and dried by being slowly heated to and maintained at 200°C in the manner stated in Example 29. After drying at 200°C, the temperature of the 10 mass is immediately and slowly heated to 540°C for 3 hours and held at this temperature for a further 2 hours for calcining.

15 The resulting calcined product has a BET surface area of 173 m<sup>2</sup>/g and an average pore size of 260 Å and may be used as a catalyst support.

#### EXAMPLE 55

##### Production of a catalyst support of attapulgite and bentonite

400 g attapulgite "ATTAGEL 50" (calculated as 20 dry material) and 21 g bentonite are dry mixed. The resulting mixture is added under intense agitation in a Z-shaped blade kneader to 1.25 litre of water containing "KLORHYDROL ACH" in an amount corresponding to 15 g Al<sub>2</sub>O<sub>3</sub> per 100 g of dry attapulgite and bentonite mixture, whereby a well-dispersed slurry is 25 formed containing 28% by weight of dry material. After this mass has been extruded in the manner mentioned above, drying is effected at 200°C in the manner stated in Example 22 and calcining in the manner stated in 30 Example 54.

The resulting calcined product has a BET surface area of 130 m<sup>2</sup>/g and an average pore size of 284 Å and may be used a catalyst support.

#### EXAMPLE 56

35 Example 55 is repeated, but instead of "KLORHYDROL ACH" water glass is used in an amount corresponding to 3.0% SiO<sub>2</sub>, calculated on the dry weight of the attapulgite and bentonite present.

The resulting calcined product has a BET surface area of  $136 \text{ m}^2/\text{g}$  and an average pore size of  $300 \text{ \AA}$  and may be used as catalyst support.

EXAMPLE 57

5      Production of a catalyst support of attapulgite and cross-linked smectite

100 g of cross-linked smectite are prepared by adding 100 g of bentonite to a solution of 90 g "KLORHYDROL ACH" in 1340 g water at  $90^\circ\text{C}$ . The suspension is kept under gentle agitation for 5 hours at  $90^\circ\text{C}$ .  
10 The filtered material is then washed three times with deionized water at  $90^\circ\text{C}$ . After the removal of the last wash water the material is dried at  $105^\circ\text{C}$  for 4 hours. By this treatment the interlayer spacing  
15  $d_{0001}$  of the cross-linked smectite is increased to 19  $\text{\AA}$ .

Example 55 is then repeated, use being made of the said cross-linked smectite instead of the bentonite.

20 The resulting calcined product has a BET surface area of  $123 \text{ m}^2/\text{g}$  and an average pore size of  $380 \text{ \AA}$  and may be used as a catalyst support.

EXAMPLE 58

Example 57 is repeated, but instead of "KLORHYDROL ACH" use is made of water glass in an amount corresponding to 3.0%  $\text{SiO}_2$ , calculated on the dry weight of  
25 attapulgite and smectite present.

The resulting calcined product has a BET surface area of  $136 \text{ m}^2/\text{g}$  and an average pore size of  $370 \text{ \AA}$  and may be used as a catalyst.

EXAMPLE 59

30      Production of a catalyst support of attapulgite

a) A well-dispersed attapulgite slurry has been prepared and spray-dried in accordance with Example 1.  
35 b) 20 g of the attapulgite spray-dried in accordance with a) is mixed with 370 g of attapulgite that has not been spray-dried and 6 g of sodium carboxyl methyl cellulose (CMC). Calculated on the dry weight,

the mixture contains 93% of attapulgite that has not been spray-dried, 2% by weight of CMC and 5% by weight of spray-dried attapulgite. This mixture is added under intense agitation in a Z-shaped blade kneader 5 to 670 g of water to form a well-dispersed slurry containing 28 % by weight of dry material.

c) This well-dispersed slurry or mass is extruded and then dried in accordance with Example 29.

d) After drying, calcining is effected by slowly raising the temperature from 200°C to 540°C for 10 3 hours, whereupon the temperature is maintained at this level for a further 2 hours.

e) After calcining, ion exchange is carried out by means of 5% by weight solution of ammonium sulphate. 15 This ion exchange treatment is effected 3 times in all. After ion exchange, the extrudate is washed 3 times with water. Both the ammonium sulphate solution and the wash water have a temperature of 60°C. Ion exchange and washing are carried out on the one hand 20 in order to remove Na<sup>+</sup> in the extrudate by ion exchange and, on the other hand, to remove any residual ash from the burning of CMC.

After the last washing with water and after filtration of the extrudate, the extrudate is heated from 25 room temperature to 150°C for 2 hours, whereupon the temperature is maintained at 150°C for a further 2 hours for drying. After that, the temperature is raised at a rate of 115°C/hour to 500°C, and the extrudate 30 is maintained at this temperature for one further hour for calcining.

The resulting product has a BET surface area of 133 m<sup>2</sup>/g and an average pore size of 300 Å, 77% of the surface area being in pores exceeding 100 Å. The product may be used as a catalyst support.

35

#### EXAMPLE 60

Example 59 is repeated, but in step b) 80 g of the spray-dried material are mixed with 300 g of attapul-

gite that has not been spray-dried and 19 g of CMC, whereby a mixture is obtained which, calculated on the dry weight, contains 74% of attapulgite that has not been spray-dried, 20% of spray-dried attapulgite 5 and 6% of CMC, said mixture being added to 670 g of water under intense agitation to form the well-dispersed slurry.

The product obtained after calcining has a BET surface area of  $132 \text{ m}^2/\text{g}$ , and average pore size of 10  $360 \text{ \AA}$ , and a pore volume of  $0.53 \text{ cm}^3/\text{g}$  and may be used as a catalyst support.

#### EXAMPLE 61

Example 59 is repeated, but step a) is omitted and in step b) 350 g of "ATTAGEL 50" are mixed with 15 6 g of CMC and 41 g of aluminium oxide ("PURAL SB"), the mixture being added to 660 g of water to form the well-dispersed slurry. Calculated on a dry basis, this well-dispersed slurry contains 88% attapulgite, 10% aluminium oxide and 2% CMC.

20 The product obtained after calcining has a BET surface area of  $141 \text{ m}^2/\text{g}$ , an average pore size of 480  $\text{\AA}$  and a pore volume of  $0.69 \text{ cm}^3/\text{g}$  and may be used as a catalyst support.

#### EXAMPLE 62

25 A well-dispersed attapulgite slurry as prepared and spray-dried according to Example 1.

21 g of this spray-dried attapulgite, 320 g of "ATTAGEL 50" and 12 g of CMC as well as 40 g of aluminium oxide ("PURAL SB") are mixed and, under intense 30 agitation, are added to 665 g of water to form a well-dispersed slurry which, calculated on a dry basis, contains 81% of attapulgite that has not been spray-dried, 5% of spray-dried attapulgite, 4% of CMC and 10% of aluminium oxide. This slurry is extruded, dried 35 and calcined in accordance with steps c), d) and e) of Example 59.

The product obtained after calcining has a BET surface area of 142 m<sup>2</sup>/g, an average pore size of 500 Å, and pore volume of 0.65 m<sup>2</sup>/g and may be used as a catalyst support.

It will thus be evident that the present invention provides a support or catalyst structure having an unusually high pore diameter coupled with a large surface area. The large surface area is concentrated to the pores having a diameter exceeding 100 Å. Typically, attapulgite having a fibre diameter of 200-300 Å will give a surface area of 100-110 m<sup>2</sup>/g. This should be compared with a surface area of about 25 m<sup>2</sup>/g for the most fine-granular kaolin clay which is frequently being used as catalyst support.

## CLAIMS

1. A filler or support for catalytically active substances, characterised in that it has a surface area of at least  $75 \text{ m}^2/\text{g}$  and an average pore diameter of at least  $100 \text{ \AA}$ , at least 75% of the surface area being in pores having a diameter exceeding  $100 \text{ \AA}$ ,  
5 and that it consists of aggregate particles having a coherent three-dimensional network structure of fibrous or strip-shaped, optionally modified mineral particles having a diameter of at least  $100 \text{ \AA}$  and having a mechanical, thermal and hydrothermal stability required for  
10 the contemplated catalytic process.

2. A filler or support as claimed in claim 1, characterised in that the mineral particles have been modified by acid treatment.

15 3. A filler or support as claimed in claim 1 or 2, characterised in that the mineral particles have a diameter of  $100\text{-}1000 \text{ \AA}$ .

20 4. A filler or support as claimed in claim 1, 2 or 3, characterised in that it has a surface area of  $75\text{-}250 \text{ m}^2/\text{g}$ .

25 5. A filler or support as claimed in any one of claims 1-4, characterised in that it consists of fibres of attapulgite, sepiolite or chrysotile or mixtures thereof and, optionally, also of minerals admixed thereto, such as montmorillonite, hectorite, vermiculite, nontronite, kaolin, or mixtures thereof.

30 6. A filler or support as claimed in any one of claims 1-5, characterised in that it contains particles of zeolite material or conventional aluminium oxide or mixtures thereof, said particles being trapped in the three-dimensional network structure.

7. A process of producing a filler or support as claimed in any one of claims 1-6, characterised in that an industrial mineral having fibrous

51

or strip-shaped structure with fibrous or strip-shaped particles of a diameter of at least 100 Å, is slurried, optionally after modification, in water and a dispersing agent to a well-dispersed slurry which then either is spray-dried to particle aggregates having a coherent three-dimensional network structure and a surface area of at least 75 m<sup>2</sup>/g as well as an average pore diameter of at least 100 Å, at least 75% of the surface area being in pores having a diameter exceeding 100 Å, or is extruded or pelletised to particle aggregates having this structure, or is first spray-dried to such particle aggregates which are then reslurried and extruded or pelletised to support articles.

8. A process as claimed in claim 7, characterised in that the mineral particles are modified by acid treatment.

9. A process as claimed in claim 7 or 8, characterised in that the well-dispersed slurry is formed of mineral particles having a diameter of 100-1000 Å.

10. A process as claimed in claim 7, 8 or 9, characterised in that the particle aggregates are given a surface area of 75-250 m<sup>2</sup>/g.

11. A process as claimed in any one of claims 7-10, characterised in that the support is formed of fibres of attapulgite, sepiolite or chrysotile or mixtures thereof and, optionally, also minerals admixed thereto, such as montmorillonite, hectorite, vermiculite, nontronite, kaolin or mixtures thereof.

12. A process as claimed in claims 7-11, characterised in that the well-dispersed slurry also is made to contain zeolite particles or conventional aluminium oxide or mixtures thereof.

13. A catalyst for catalytic hydroprocessing, hydrogenation or cracking of hydrocarbons, characterised in that it consists of a catalyst support as claimed in any one of claims 1-6, and a surface coating

of a catalytically active substance on the fibrous or strip-shaped particles of the catalyst support.

14. A catalyst as claimed in claim 13, characterised in that the fibrous or strip-shaped particles of the support are coated with colloidal particles, the surface of which is coated with the catalytically active substance.

15. A catalyst as claimed in claim 13 or 14, characterised in that the surface coating of catalytically active substance consists of a metal from the platinum group, gold or silver, cobalt sulphide, nickel sulphide, molybdenum sulphide + cobalt sulphide, molybdenum sulphide + nickel sulphide, tungsten sulphide + cobalt sulphide, or tungsten sulphide + nickel sulphide.

16. A catalyst as claimed in claim 13, characterised in that the fibrous or strip-shaped particles have a surface coating of aluminium silicate or alkali aluminium silicate converted into catalytically active form by ion exchange with hydrogen ions or ions of rare earth metals.

17. A catalyst as claimed in any one of claims 13-16, characterised in that it contains particles of zeolite material trapped in the three-dimensional network structure.

18. A catalyst as claimed in any one of claims 13-17, characterised in that it contains particles of minerals, such as montmorillonite, hectorite, vermiculite, nontronite, kaolin or mixtures thereof, trapped in the three-dimensional network structure, said minerals being admixed in an amount of at most 50% by weight.

19. A catalyst as claimed in claim 17 or 18, characterised in that the zeolite in the catalyst is 0.5-75% by weight, preferably 10-75% by weight, especially 25-60% by weight.

20. A catalyst as claimed in claim 17, 18 or 19, characterised in that the zeolite particles

have a particle size of 0.1-5 µm, preferably 0.5-5 µm or 0.5-3 µm.

21. A process of producing a catalyst as claimed in any one of claims 13-20, in which process a catalyst support is formed and coated with a catalytically active substance, characterised in that the catalyst support is prepared in accordance with any one of claims 7-12, and that the catalytically active substance or a precursor thereof is applied as a surface coating on the fibrous or strip-shaped particles of the support prior to or after spray-drying, extrusion or pelletisation of the support particles.

22. A process as claimed in claim 21, characterised in that the fibrous or strip-shaped particles of the slurry are coated with a homogeneous layer of aluminium silicate prior to spray-drying, and that the aluminium silicate is converted into catalytically active form by ion exchange with hydrogen ions or ions of rare earth metals.

23. A process as claimed in claim 21 or 22, characterised in that the fibrous or strip-shaped particles prior to or after spray-drying, extrusion or pelletisation are coated with aluminium silicate or alkali aluminium silicate or with silicic acid sol particles, the surface of which has been modified by means of an aluminate and an alkali aluminate, respectively, to aluminium silicate and alkali aluminium silicate, respectively, and that the aluminium silicate is converted into catalytically active form by ion exchange with hydrogen ions or ions of rare earth metals.

24. A process as claimed in claim 21, characterised in that the surface coating of catalytically active substance on the surface of the fibrous or strip-shaped particles is formed of a metal from the platinum group, gold or silver, cobalt sulphide, nickel sulphide, molybdenum sulphide + cobalt sulphide, molybdenum sulphide + nickel sulphide, tungsten sulphide

54

+ cobalt sulphide or tungsten sulphide + nickel sulphide.

25. Use of a catalyst as claimed in any one of claims 13-20, for hydroprocessing, hydrogenation or catalytic cracking of hydrocarbon fractions, especially heavy residual fractions.

5

# INTERNATIONAL SEARCH REPORT

International Application No PCT/SE85/00037

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) \*

According to International Patent Classification (IPC) or to both National Classification and IPC4

B 01 J 35/10, 21/16, 29/28

## II. FIELDS SEARCHED

Minimum Documentation Searched ?

Classification System	Classification Symbols
IPC 4	B 01 J 20/28, 21/04, 21/16, 23/38-23/52, 27/04, 29/28 35/00, 35/04-35/10, 37/02
US CL	<u>252</u> :439, 460, 477; <u>502</u> :60, 72, 220-233

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched \*

SE, NO, DK, FI classes as above

## III. DOCUMENTS CONSIDERED TO BE RELEVANT\*

Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages 12	Relevant to Claim No. 13
X	SE, B, 6912751-2 (STAMICARBON NV) 11 June 1979	1-25
X	SE, B, 345 393 (STAMICARBON NV) 29 May 1972	1-25
X	WO, A, 81/02688 (YTKEMISKA INST) 1 October 1981 & EP, 0055257 US, 4425261	1-25
X	DE, B, 1 958 952 (STAMICARBON BV) 25 January 1974 & NL, 6816777 FR, 2023994 GB, 1282138 BE, 742099 CH, 551800 AT, 300737 JP, 54155189 SE, 370332	1-25
	... / ...	

\* Special categories of cited documents: 10

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"A" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

1985-04-01

Date of Mailing of this International Search Report

1985-04-04

International Searching Authority

Swedish Patent Office

Signature of Authorized Officer

*Britt-Marie Lundell*  
Britt-Marie Lundell

L.E.

## III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category*	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
X	DE, B, 1 963 827 (STAMICARBON BV) 19 October 1978 & NL, 6818337 FR, 2026748 GB, 1256610 BE, 743395	1-25
A	SE, B, 7310110-7 (HOECHST AG) 14 March 1977	
A	SE, B, 7204618-8 (SNAM PROGETTI SPA) 28 March 1977	
A	DE, B, 2 530 759 (RUHRCHEMIE AG) 24 June 1976	
A	DE, A, 2 219 736 (NIPPON OIL) 9 November 1972	
A	DE, A, 1 912 012 (RIRDLER-SÜDCHEMIE KATALYSATOR GMBH) 17 September 1970	
A	EP, A, 15 801 (RHONE-POULENC IND.) 17 September 1980	
A	DE, C, 3 003 361 (UOP INC.) 21 October 1982	
A	DE, B, 1 542 185 (WR GRACE CO) 25 November 1975	
Y	GB, A, 1 485 370 (UNITED KINGDOM ATOMIC ENERGY AUTHORITY) 8 September 1977	
Y	GB, A, 2 090 766 (CHEVRON RESEARCH) 21 July 1982 & DE, 3146306 US, 4364857 CA, 1168210 JP, 57140646 US, 4358400	
Y	US, A, 4 421 699 (NIPPON SOKEN) 20 December 1983 & JP, 56145171	
E	EP, A, 123 293 (EIDU PONT DE NEMOURS AND COMP) 31 October 1984	
E	SE, B, 8205919-7 (EKA AB) 28 January 1985	

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record.**

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

**BLACK BORDERS**

**IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

**FADED TEXT OR DRAWING**

**BLURRED OR ILLEGIBLE TEXT OR DRAWING**

**SKEWED/SLANTED IMAGES**

**COLOR OR BLACK AND WHITE PHOTOGRAPHS**

**GRAY SCALE DOCUMENTS**

**LINES OR MARKS ON ORIGINAL DOCUMENT**

**REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

**OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**

THIS PAGE BLANK (USPTO)